

Mean Amplitudes of Vibration of the Novel SbF_7^{2-} , BiF_7^{2-} and Dianions

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Mean amplitudes of vibration of the recently reported pentagonal bipyramidal SbF_7^{2-} and BiF_7^{2-} dianions were calculated from vibrational spectroscopic data, in the temperature range between 0 and 1000 K. The results are briefly discussed and some comparisons with related species are made.

Key words: Mean Amplitudes of Vibration; SbF_7^{2-} ; BiF_7^{2-} ; Temperature Dependence; Bond Characteristics.

Relatively few examples of molecules and ions are known that present pentagonal bipyramidal and related structures with five-fold symmetry. Only very recently a certain number of anionic species structurally related to this basic geometry could be prepared and characterized in detail. They include XeF_5^- [1] and IF_5^{2-} [2] (pentagonal planar geometry); XeOF_5^- [3] and IOF_5^{2-} [4] (pentagonal pyramidal geometry) and IOF_6^- [5–7], TeOF_6^{2-} [6] and TeF_7^- [8] (pentagonal bipyramidal geometry).

Last year some salts containing the novel SbF_7^{2-} and BiF_7^{2-} dianions could also be prepared and characterized. They possess a pentagonal bipyramidal structure with D_{5h} symmetry, similar to that of IF_7 [9].

As a continuation of our studies devoted to a better characterization of the bond and vibrational properties of species of this type [10–15], we have now undertaken a calculation of the mean amplitudes of vibration of these two novel and interesting species.

The calculations of the mean amplitudes of vibration were performed with the so-called “method of the characteristic vibrations” of Müller et al. [16–18] and using the recently reported vibrational spectroscopic data [9]. The following structure parameters were used: $d(\text{Sb-F}_{\text{ax}}) = 1.89 \text{ \AA}$; $d(\text{Sb-F}_{\text{eq}}) = 1.97 \text{ \AA}$; $d(\text{Bi-F}_{\text{ax}}) = 1.96 \text{ \AA}$; $d(\text{Bi-F}_{\text{eq}}) = 2.03 \text{ \AA}$; the $\text{F}_{\text{ax}}\text{-M-F}_{\text{eq}}$ angles were considered equal to 90° and those in the equatorial plane equal to 72° [9].

The calculated mean amplitudes of vibration for the two investigated species, in the temperature range between 0 and 1000 K, are shown in Tables 1 and 2.

An analysis of these values immediately shows that the Sb-F bonds are somewhat stronger than the Bi-F ones and also, in both cases, the axial bonds are stronger than the equatorial bonds. These results are in excellent agreement with the respective force constants [9] and also with the bond model proposed for these species [8, 9, 19, 20]. It involves a planar, delocalized p_{xy} hybrid orbital of the central atom for the formation of five equatorial, semi ionic, 6-center, 10-electron bonds and an sp_z hybrid for the formation of two mainly covalent axial bonds.

A comparison of the mean amplitudes values of SbF_7^{2-} with those of its isoelectronic species TeF_7^- and IF_7 [13] shows the expected behaviour for such a series, for which the bond strength of the bonds should increase with increasing formal charge of the central atom. This bond reinforcement generates a diminution of the mean amplitude values when going from SbF_7^{2-} to TeF_7^- and to IF_7 ,

Table 1. Mean amplitudes of vibration (\AA) for SbF_7^{2-} .

T/K	$u_{\text{Sb-F}(\text{eq})}$	$u_{\text{Sb-F}(\text{ax})}$	$u_{\text{F}\dots\text{F}(\text{eq.sh})}$	$u_{\text{F}\dots\text{F}(\text{eq.lg})}$	$u_{\text{F}_{\text{eq}}\dots\text{F}_{\text{ax}}}$
0	0.0454	0.0409	0.067	0.060	0.062
100	0.0454	0.0409	0.067	0.060	0.063
200	0.0467	0.0414	0.071	0.062	0.068
298.16	0.0497	0.0431	0.079	0.067	0.075
300	0.0497	0.0431	0.079	0.067	0.076
400	0.0537	0.0457	0.087	0.072	0.084
500	0.0579	0.0486	0.094	0.078	0.092
600	0.0621	0.0517	0.102	0.084	0.099
700	0.0662	0.0547	0.109	0.089	0.106
800	0.0709	0.0577	0.116	0.095	0.113
900	0.0739	0.0607	0.123	0.100	0.120
1000	0.0775	0.0635	0.129	0.105	0.126

Table 2. Mean amplitudes of vibration (\AA) for BiF_7^{2-} .

T/K	$u_{\text{Bi-F}(\text{eq})}$	$u_{\text{Bi-F}(\text{ax})}$	$u_{\text{F}\dots\text{F}(\text{eq.sh})}$	$u_{\text{F}\dots\text{F}(\text{eq.lg})}$	$u_{\text{F}_{\text{eq}}\dots\text{F}_{\text{ax}}}$
0	0.0456	0.0416	0.069	0.061	0.065
100	0.0457	0.0416	0.070	0.061	0.065
200	0.0457	0.0424	0.075	0.063	0.072
298.16	0.0509	0.0446	0.083	0.068	0.080
300	0.0510	0.0446	0.083	0.068	0.080
400	0.0554	0.0477	0.092	0.073	0.089
500	0.0599	0.0510	0.101	0.079	0.098
600	0.0644	0.0545	0.109	0.085	0.106
700	0.0687	0.0579	0.116	0.091	0.114
800	0.0729	0.0611	0.124	0.096	0.121
900	0.0769	0.0644	0.131	0.101	0.128
1000	0.0807	0.0675	0.138	0.107	0.135

as it can be seen below, from the values calculated at 298.16 K:

$$\text{SbF}_7^-: u_{\text{Sb-F}(\text{eq})} = 0.0497 \text{ \AA}; u_{\text{Sb-F}(\text{ax})} = 0.0431 \text{ \AA},$$

$$\text{TeF}_7^-: u_{\text{Te-F}(\text{eq})} = 0.0452 \text{ \AA}; u_{\text{Te-F}(\text{ax})} = 0.0405 \text{ \AA},$$

$$\text{IF}_7^-: u_{\text{I-F}(\text{eq})} = 0.0430 \text{ \AA}; u_{\text{I-F}(\text{ax})} = 0.0390 \text{ \AA}.$$

A further analysis of the data presented in Tables 1 and 2 shows that the temperature dependence of the Sb-F and Bi-F bonds is similar although somewhat larger for the bismuth anion. On the other hand, for both anions

the mean amplitudes of vibration for the non-bonded pairs follow the same trend: $F \cdots F(\text{eq/long}) < F_{\text{eq}} \cdots F_{\text{ax}} < F \cdots F(\text{eq/short})$. This trend is similar as those previously observed for TeF_7^- and IF_7^- [13].

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